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Chilled ammonia process for CO_2 capture

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Abstract

The chilled ammonia process absorbs the CO_2 at low temperature (2-10°C). The heat of absorption of carbon dioxide by ammonia is significantly lower than for amines. In addition, degradation problems can be avoided and a high carbon dioxide capacity is achieved. Hence, this process shows good perspectives for decreasing the energy requirement. However, a scientific understanding of the processes is required. The properties of the NH_3-CO_2-H_2O system were described using the Extended UNIQUAC electrolyte model developed by Thomsen and Rasmussen in a temperature range from 0 to 110°C and pressure up to 100 bars [1]. The results show that solid phases consisting of ammonium carbonate and bicarbonate are formed in the absorber. The energy requirements in the absorber and in the desorber have been studied. The enthalpy calculations show that an energy requirement for the desorber lower than 2 GJ/ton CO_2 can be reached.

CO_2 capture; Chilled ammonia process; Extended UNIQUAC model; Aqueous ammonia, Carbon dioxide; CO_2; NH_3; H_2O

1. Introduction

The proportion of carbon dioxide emissions from power production is very significant in industrialized countries. In Denmark, in 2004, they represented 61% of the total CO_2 emissions [3]. Therefore, regarding the reduction objectives endorsed by many governments, efforts are being made to develop technologies allowing the decrease of the emissions from the power plants. Carbon dioxide capture implies separating the CO_2 from the flue gases from a power plant or other industry instead of releasing the CO_2 in the atmosphere. Several methods can be used to capture CO_2 from coal-fired power plants. Post-combustion techniques separate the carbon dioxide from the flue gas after a traditional combustion process. The main advantage of such technique is that the combustion at the power plant is unaltered, so the process can be implemented on existing power plants. Amine solutions have been commonly used for the commercial production of CO_2 and have been tested for CO_2 capture on pilot scale. However such technologies require a large amount of energy, especially in the desorption part of the process [4]. In addition, the use of amines entails some problems related to solvent degradation and corrosion [5, 6]. Therefore, new

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alternatives for post-combustion capture are searched for. Processes using aqueous ammonia as solvent are some of the promising alternatives. The ammonia process is found in two variants, depending on the temperature of absorption. The first variant absorbs the CO_2 at low temperature (2-10°C) and is therefore called chilled ammonia process. The low temperature process has the advantage of decreasing the ammonia slip in the absorber and decreasing the flue gas volume. This process allows precipitation of several ammonium carbonate compounds in the absorber. The second process absorbs CO_2 at ambient temperature (25-40°C) and does not allow precipitation. This study focuses on the chilled ammonia process for CO_2 capture.

2. Description of the patented process

The use of chilled ammonia to capture carbon dioxide was patented in 2006 by Eli Gal [2]. The process described in the patent requires several steps. First, the purpose of the process is to absorb the carbon dioxide at a low temperature. The patent indicates a temperature range from 0 to 20°C, and preferably from 0 to 10°C. Hence, it is first necessary to cool down the flue gas that contains the CO_2. This is done by using Direct Contact Coolers at the entrance of the process. The temperature of the gas that leaves the cooling subsystem is comprised between 0 and 10°C. This stream contains low moisture and almost no particulate matter, acidic or volatile species. Indeed, the low temperature decreases the vapor pressure of these compounds as it entails their condensation into the water.

Then, the flue gas enters the CO_2 capture and regeneration subsystem. This subsystem consists, like the capture processes using amines, of absorption and desorption columns.

The cold flue gas enters the bottom of the absorber while the CO_2-lean stream enters the top of it. The CO_2-lean stream is mainly composed of water, ammonia and carbon dioxide. The mass fraction of ammonia in the solvent is typically up to 28wt%. The pressure in the absorber should be close to atmospheric pressure, while the temperature should be in the range 0-20°C, and preferably 0-10°C. This low temperature prevents the ammonia from evaporating. According to the patent, the CO_2-lean stream should have a CO_2 loading (the ratio of the number of mole of carbon dioxide and ammonia in their various aqueous forms) between 0.25 and 0.67, and preferably between 0.33 and 0.67. A low CO_2 loading in the top of the absorber where the CO_2-lean stream is fed in increases the vapor pressure of ammonia which implies its evaporation. On the other hand, a high CO_2 loading for the CO_2-lean stream decreases the efficiency of the absorption.

Under the conditions described above and according to the patent, more than 90% of the CO_2 from the flue gas can be captured. The cleaned gas stream can leave the absorber by its top. This stream contains residual ammonia, which is washed out by using cold water and an acidic solution. The treated stream is reintroduced into the system. The cleaned gas mainly contains nitrogen, oxygen and a low concentration of carbon dioxide.

The CO_2-rich stream leaves the bottom of the absorber. It might be composed of a solid and a liquid phase. Indeed, at this temperature and under those conditions, the solubility limits may be reached. Hence, the CO_2-rich stream is a slurry. Its CO_2 loading is between 0.5 and 1, and preferably between 0.67 and 1. The patent mentions that a part of the CO_2-rich stream could be recycled to the absorber in order to increase the CO_2 loading of the CO_2-rich stream by producing more solids.

The CO_2-rich stream is pressurized and pumped to a heat exchanger where its temperature increases, and then sent to the desorber using a high pressure pump. The desorber temperature is in the range of 50-200°C, and preferably 100-150°C while the pressure is in the range of 2-136 atmospheres. Under those conditions, the vaporization of ammonia and water implied by the high temperature is reduced. The conditions cause CO_2 to evaporate from the solution. It leaves the top of the desorber as a relatively clean and high pressure stream. The water vapor and the ammonia that are contained in this stream can be recovered by cold washing, possibly using weak acid to increase the efficiency.

The desorption reaction is endothermic, but the energy that has to be supplied is much lower than for MEA or other amines according to the patent. This energy highly depends on the composition of the CO_2-rich stream that enters the desorber. In addition, the pure CO_2 stream that is obtained with this process is already at high pressure.

Hence, a part of the energy needed to compress this stream is saved. In addition, the high pressure desorption is a way to limit the vaporization of water, which entails a lower energy consumption.

3. Description of the model

This study uses the extended UNIQUAC thermodynamic model developed for the CO_2-NH_3-H_2O system by Thomsen and Rasmussen [1]. It calculates the activity coefficient for the liquid phase using the extended UNIQUAC model, and the gas phase fugacity using the Soave-Redlich-Kwong (SRK) equation for the volatile compounds. The model only requires binary interaction parameters, UNIQUAC surface area and volume parameters. It is based on more than 2000 experimental data points on this system in the IVC-SEP electrolyte data bank, including thermal properties and solid-liquid equilibrium. These data were used to fit the parameters. The analysis of the CO_2-NH_3-H_2O system implies the study of several equilibrium processes. The following reactions are considered in the model:

Speciation equilibria

$$NH_3(aq)+H_2O \longleftrightarrow NH_4^+ + OH^- \quad (1)$$

$$CO_2(aq)+H_2O(l) \longleftrightarrow HCO_3^- + H^+ \quad (2)$$

$$HCO_3^- \longleftrightarrow CO_3^{2-} + H^+ \quad (3)$$

$$H_2O(l) \longleftrightarrow OH^- + H^+ \quad (4)$$

$$NH_3(aq)+HCO_3^- \longleftrightarrow NH_2COO^- + H_2O(l) \quad (5)$$

Vapor-liquid equilibria

$$CO_2(g) \longleftrightarrow CO_2(aq) \quad (6)$$

$$NH_3(g) \longleftrightarrow NH_3(aq) \quad (7)$$

$$H_2O(g) \longleftrightarrow H_2O(l) \quad (8)$$

Liquid-solid equilibria

$$NH_4^+ + HCO_3^- \longleftrightarrow NH_4HCO_3(s) \quad (9)$$

$$NH_4^+ + NH_2COO^- \longleftrightarrow NH_2COONH_4(s) \quad (10)$$

$$2NH_4^+ + CO_3^{2-} + H_2O \longleftrightarrow (NH_4)_2CO_3.H_2O(s) \quad (11)$$

$$H_2O(l) \longleftrightarrow H_2O(s) \quad (12)$$

$$4NH_4^+ + CO_3^{2-} + 2HCO_3^- \longleftrightarrow (NH_4)_2CO_3.2NH_4HCO_3(s) \quad (13)$$

Hence, five different solids can be formed during the process:

- Ammonium bicarbonate: NH_4HCO_3
- Ammonium carbonate: $(NH_4)_2CO_3.H_2O$
- Ammonium carbamate: NH_2COONH_4
- Sesqui-carbonate: $(NH_4)_2CO_3 \cdot 2NH_4HCO_3$
- Ice: H_2O

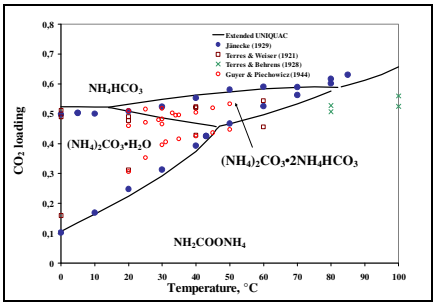


Figure 1: Phase diagram of the CO_2-NH_3-H_2O system

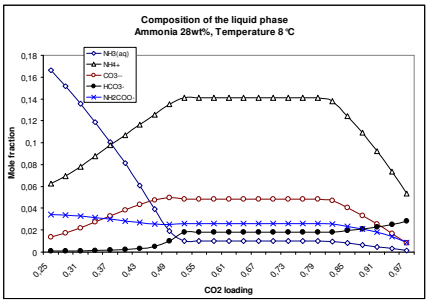
Figure 1 shows which solid phase can precipitate at various temperatures and CO_2 loadings calculated with the model. Some of the experimental data are marked in the diagram [7, 8, 9 and 10], showing the good agreement between the model and the experimental data.

The model has shown to be capable of describing accurately the vapor-liquid-solid equilibria and thermal properties for the CO_2-NH_3-H_2O system for a wide range of concentration (up to 80 molal NH_3), for a temperature in the range of 0-110°C and for a pressure up to 100 bars [1].

4. Composition of the process streams

Based on the software and on the information from the patent of the process, the equilibrium composition of the different streams of the process has been studied. The results shown here describe the compositions of the streams in the absorber and in the desorber. A typical initial mass fraction of ammonia in the solvent is 28wt%. This value has been used in this study.

In the absorber, the temperature should be in the range of 0-20°C, and preferably 0-10°C. The CO_2 loading of the CO_2-lean stream (lean CO_2 loading) is in the range of 0.25-0.67, and the one of the CO_2-rich stream (rich CO_2 loading) in the range of 0.5-1. Therefore it is relevant to study the influence of the CO_2 loading from 0.25 to 0.97 by maintaining the temperature at 8°C and by using an initial mass fraction of ammonia in the solvent of 28wt%. Hence, the molality of ammonia in the solvent is 22.83 mol/kg H_2O, and the molality of CO_2 varies from 5.71 to 22.1 mol/kg H_2O. This equilibrium study gives an overview of the species that appear in the absorber. Figure 2, Figure 3 and Figure 4 show respectively the composition of the liquid phase, the nature and amount of solid phases and bubble point pressures of a 28wt% ammonia solvent at a temperature of 8°C as a function of the CO_2 loading.



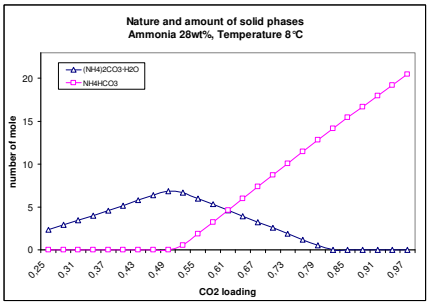


Figure 2: Composition of the liquid phase of a 28wt% ammonia solvent with a temperature of 8°C as a function of the CO_2 loading
Figure 3: Nature and amount of solid phases of a 28wt% ammonia solvent with a temperature of 8°C as a function of the CO_2 loading

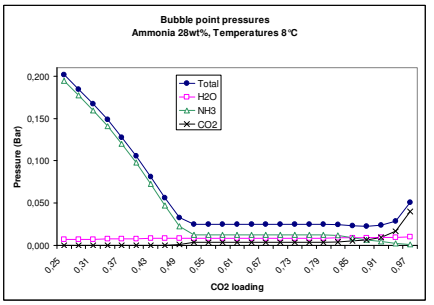
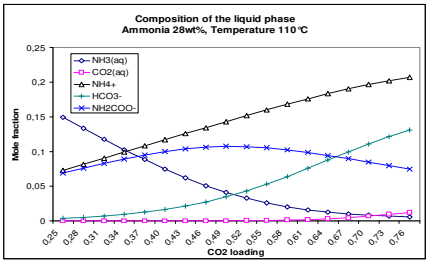


Figure 4: Bubble point pressures of a 28wt% ammonia solvent with a temperature of 8°C as a function of the CO_2 loading

It can be seen from Figure 2 that the CO_2 loading has a very significant influence on the composition of the liquid phase. The discontinuities that are observed correspond to the appearance of the ammonium bicarbonate and disappearance of the ammonium carbonate solid phases at loadings of 0.50 and 0.85. The composition of the solution and the pH are very stable for a loading between these values. Figure 3 shows that at 8°C, a solid phase that consists of ammonium carbonate is present for CO_2 loadings up to 0.85. For loadings higher than 0.5, another solid phase that consists of ammonium bicarbonate appears. This result is in agreement with the phase diagram presented in Figure 1, which shows that increasing the loading entails the formation of ammonium bicarbonate and the decrease of the amount of ammonium carbonate. Figure 4 shows that at low CO_2 loadings (in the top of the absorber), the mole fraction of ammonia in the gas phase is very high. Therefore, it is likely that quite some ammonia is swept along in the pure gas stream that leaves the absorber. Hence, a washing section must be considered to limit the emission of ammonia.

A similar study was performed to analyze the composition of the stream in the desorber. The same initial mass fraction of ammonia was chosen (28wt%). According to the patent, the desorption preferably occurs at temperatures in the range of 100-150°C. The CO_2 loading decreases in the stripper as the carbon dioxide is desorbed there. The influence of this parameter on the composition of the stream in the stripper is studied in Figure 5, Figure 6 and Figure 7. A temperature of 110°C was chosen in the study. The CO_2 loading was varied from 0.25 to 0.77. The model is not accurate for pressures higher than 100 bars that are obtained for higher loadings.



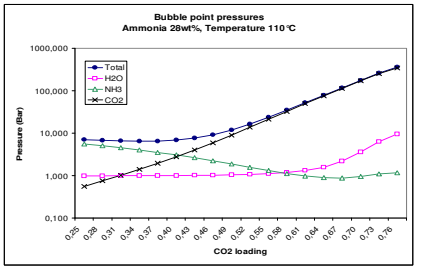


Figure 5: Composition of the liquid phase of a 28wt% ammonia solvent with a temperature of 110°C as a function of CO_2 loading
Figure 6: Bubble point pressures of a 28wt% ammonia solvent with a temperature of 110°C as a function of the CO_2 loading

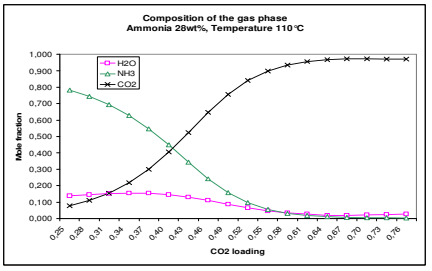


Figure 7: Composition of the bubble point gas phase of a 28wt% ammonia solvent with a temperature of 110°C as a function of the CO_2 loading

According to these calculations, no solid phase is present at 110°C. Therefore, all solids are dissolved in the heat exchanger, which is in accordance with the patent. It can be seen from Figure 6 that the pressure can reach high values, especially when the CO_2 loading is high. It should be noticed that a logarithmic scale is used for the ordinate axis. Figure 7 shows that for high CO_2 loading, the mole fraction of carbon dioxide in the gas phase is very close to 1. Providing that the CO_2-rich stream that enters the stripper has a high CO_2 loading, this figure shows that at high temperature, it is possible to get a pressurized and nearly pure CO_2 stream. The use of a condenser and a washing

section allow the cleaning of the pure CO_2 stream from water and ammonia. Hence, some energy savings can be made during the compression of the CO_2 stream before it is transported and sequestrated.

5. Energy requirement

The energy requirement, and especially the heat required in the desorber, is a key parameter of a capture process. The use of ammonia is supposed to lower the energy requirement. The heat required in the desorber was studied. Figure 8 shows a schematic flow sheet of the stripping part of the process. This study takes into account the amounts of water and ammonia that are swept along in the gas phase and eventually pumped to the desorber after the pure CO_2 stream passes through a condenser and a washing section.

A reference configuration has been set up according to the information from the patent. The main assumptions are summed up in Table 1.

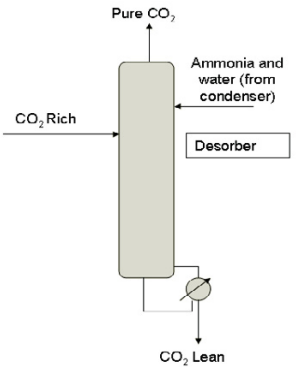


Table 1: Description of the stripper reference configuration

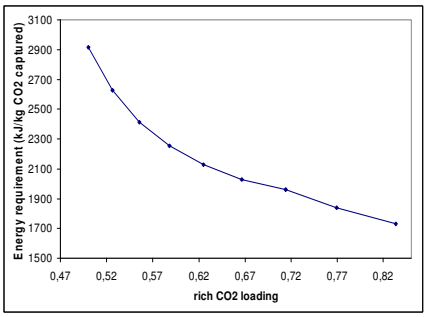
NH_3 init wt%	T CO_2-Lean	T CO_2-Rich	T Pure CO_2	Lean CO_2 loading	Rich CO_2 loading	T H_2O + NH_3 from condenser
28	110°C	90°C	110°C	0.33	0.67	25°C

The energy requirement in the stripper is calculated according to the following formula. It is expressed in kJ/kg CO_2 captured.

$$ER_{des} = \frac{H\,CO_2\,Lean + H\,Pure\,CO_2 - H\,CO_2\,Rich - H\,NH_3/H_2O\,condenser}{Amount\ of\ CO_2\ in\ pure\ CO_2 stream * MW(CO_2)}$$

Figure 8: Flow sheet of the stripper

Different parameters were modified individually in order to assess their influence. Figure 9 and Figure 10 shows the influence of the rich CO_2 loading and of the initial mass fraction of ammonia on the energy requirement in the desorber. Figure 9 shows that the energy requirement decreases as the rich CO_2 loading decreases. Figure 10 shows that the energy requirement decreases for an initial mass fraction of ammonia from 0.16 to 0.28, and increases again for higher mass fractions. This increase can be explained by the fact that for this high concentration of ammonia, a temperature of 90°C is not high enough to dissolve all the precipitate contained in the rich CO_2 stream coming from the absorber and the heat exchanger.



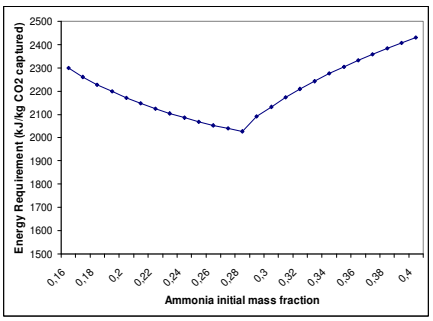


Figure 9: Energy requirement as a function of the loading of the CO_2-rich stream, at a constant mass fraction of 28% ammonia.
Figure 10: Energy requirement as a function of the initial mass fraction of ammonia, at a constant rich CO_2 loading of 0.67

The CASTOR project that consists of a pilot capture plant using aqueous amines resulted in an energy consumption in the stripper of about 3700 kJ/kg CO_2 captured for MEA, with a capture efficiency of 90% [11]. Hence, our study shows that based on the equilibrium calculations, the use of ammonia as a solvent is a way to achieve very significant decreases in the energy consumption in the desorber. In addition, the configuration studied here can be further optimized to reduce the energy requirement. Moreover, as mentioned above, the CO_2 stream that is obtained at the end of the process is pressurized when ammonia is used, which would result in additional energy savings during compression of the carbon dioxide. However, it must be noticed that this study does not take into account the additional energy required to lower the temperature of both the flue gas (including the resulting condensation of water) and the CO_2-lean stream entering the absorber. Moreover, it should be realized that extensive cooling of the absorber is required for keeping a low temperature. For a similar reference configuration as shown for the desorber in Table 1, an amount of 2050 kJ/kg CO_2 produced heat was calculated for the absorber.

Moreover, issues like the handling of the slurries and kinetics of absorption will be critical issues that have to be addressed.

6. Future work

Currently, the thermodynamic model used is being updated. The new version of the model is based on additional experimental vapor-liquid equilibria data in order to enlarge the range temperature where the model is valid. In addition, the data from the measurement of the enthalpy change from partial evaporation of CO_2-NH_3-H_2O mixtures, by Rumpf et al. [12] have been added to the data bank. Furthermore, the new version of the model is able to calculate the residual enthalpy from the gas phase, calculated with equations derived from the SRK equation of state. This allows for determining more accurately the total enthalpy of the gas phase, and therefore obtaining more precise energy requirements calculations. A new set of parameters is being determined based on all the data, using the same optimization method as the one used by Thomsen et al. [1] in the previous version of the model. According to the preliminary results from the upgraded model, the energy requirement in the desorber calculated is even slightly lower than the one calculated with the original model.

7. Summary and conclusion

The CO_2 capture process using chilled ammonia is a post-combustion process that has been patented in 2006. It consists of absorbing the carbon dioxide from the flue gas of a power plant at low temperature (0-20°C) using ammonia as solvent. In this temperature range precipitation occurs in the absorber. The desorption is made at high temperature (100-200°C).

The extended UNIQUAC model developed by Thomsen and Rasmussen [1] was used to describe the equilibrium of the CO_2-NH_3-H_2O system. This model is valid for temperatures in the range 0-110°C and for molalities in the range 0-80mol/kg H_2O. Thanks to the indications from the patent, it was possible to describe the composition of the different streams. This study showed the presence of precipitates in the absorber, and the formation of ammonium bicarbonate from the ammonium carbonate present in the CO_2-lean stream during the absorption process. The equilibrium calculation of the gas phase in the absorber shows a high mole fraction of ammonia. Hence, some cleaning subsystems at the top of the absorber should be considered in order to avoid the emission of ammonia. It was also shown that the pure CO_2 stream that leaves the desorber column is pressurized. From an energetic point of view, a reference configuration was used to assess the energy requirement both in the absorber and in the desorber. Based on equilibrium calculations, this study showed that the chilled ammonia process allows for a significant reduction of the energy consumption in the desorber compared to the energy consumption of the process using amines.

8. Acknowledgement

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